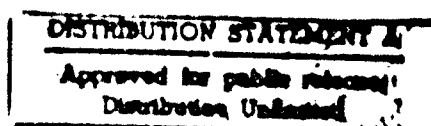CRREL

In-Situ Detection of Contaminant Plumes in Ground Water

W. Rudolf Seitz

August 1990

AD-A228 973

DTIC
ELECTE
NOV 0 9 1990
S
B
D

20030206200

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

Special Report 90-27

U.S. Army Corps of Engineers
Cold Regions Research &
Engineering Laboratory

In-Situ Detection of Contaminant Plumes in Ground Water

W. Rudolf Seitz

August 1990

PREFACE

This report was prepared by Dr. W. Rudolf Seitz, Professor, of the Department of Chemistry, University of New Hampshire. Funding for this research was provided by the U.S. Army Toxic and Hazardous Materials Agency (THAMA) through the U.S. Army Engineer Waterways Experiment Station (WES) under WESAM 89-110.

The author thanks Ronald Atkins, Dr. I.K. Iskandar, Dr. Olufemi Ayorinde and Dr. Austin Hogan of CRREL, and Paul Lurk of THAMA, Project Monitor, for their technical review of this report, and Dr. Thomas Jenkins for helpful discussion.

The contents of this report are not to be used for advertising or promotional purposes. Citation of brand names does not constitute an official endorsement or approval of the use of such commercial products.

In-Situ Detection of Contaminant Plumes
in Ground Water

W. RUDOLF SEITZ

INTRODUCTION

The cone penetrometer provides a cost-effective method for characterizing subsurface soil stratification and determining permeability. The greater the permeability, the greater the ability for ground water and contaminants to migrate. In addition, a penetrometer equipped with additional instrumentation could attempt to verify the presence of contaminants and determine the gradient and boundary of a plume. The ability to define the boundary of a plume depends on the levels that can be detected by the instrumentation and the accuracy of sampling and of the method itself. Since the outer limit or boundary of a plume as established by the regulatory community represents the legal limit of the plume, any instrument that can verify the presence of contaminants can assist in plume characterization.

This report reviews the current status of in-situ sensing technologies that can potentially be used in conjunction with the cone penetrometer to detect the following types of plumes in ground water:

1. Petroleum fuels (aliphatic and aromatic hydrocarbons).
2. Chlorinated hydrocarbons.
3. Nitrated organics, primarily explosives.
4. Heavy metal ions (mainly from electroplating wastes).

The cone penetrometer can be most effectively used in combination with real-time continuous measurement to get a profile of contaminant concentration vs depth. However, the site characterization and analysis penetrometer system (SCAPS) can also be used in an attached sampling monitor mode and an unattached sampling/monitoring mode.

Emphasis in this report will be on in-situ spectroscopic measurements through fiber optics. The potential for using fiber optics for in-situ measurements in ground water was recognized several years ago (Hirschfeld et al. 1983, Hirschfeld et al. 1984). More recent progress in developing systems for in-situ analysis is summarized in recent review articles (Angel 1987, Seitz 1988, Wolfbeis 1988). The rationale for using fiber optics for in-situ environmental analysis has recently been considered by Eccles and Eastwood (1989). It is assumed in this report that a large volume of sample is available such that detection limits are established by the ability to measure low concentrations rather than the ability to detect absolute amounts.

FIBER OPTICS AND SPECTROSCOPY

Traditionally, most spectroscopic methods of analysis have been laboratory oriented. The sample has been brought back to the laboratory and presented to the spectrometer in a controlled manner. Often the sample is treated, e.g., with pH adjustment or addition of color-forming reactants, to convert it to a form that is more readily measured spectroscopically.

Recently, developments in fiber optic technology have stimulated interest in applying spectroscopy in situ using optical fibers to conduct light between the sample and the spectrometer. In many contexts the spectrometer can remain in the laboratory and be coupled to remote sampling sites without serious losses in light intensity. In the case of spectroscopic measurements coupled to the cone penetrometer, it is envisioned that the spectrometer would be permanently installed in a mobile laboratory.

Plastic-clad silica is the preferred optical fiber for measurements in the visible and ultraviolet regions of the electromagnetic spectrum (Skutnik et al. 1988). It is

available with numerical apertures as high as 0.48 and transmits in the ultraviolet down to 220 nm. Attenuation by the fiber increases as wavelength decreases, complicating remote measurements in the ultraviolet below 300 nm. Plastic-clad silica fibers are commonly available with core diameters of 0.20, 0.60 and 1.0 mm. The larger diameter fibers allow for greatly enhanced light transmission but are significantly more expensive. Fibers with 0.60-mm core diameters provide a good compromise between cost and throughput, and have been used for remote laser-induced fluorescence measurements of aromatic hydrocarbons in water (Chudyk et al. 1985). Glass fibers developed for communications applications have extraordinarily high transmission in the near-infrared region of the spectrum but have low numerical apertures and do not transmit below 380 nm.

There is considerable current interest in developing fibers that conduct light at longer wavelengths, extending further into the infrared region of the spectrum (Drexhage and Moynihan 1988). However, while developments in this area may enhance the capabilities of infrared spectroscopy, this technique is not sensitive enough to detect contaminant plumes in ground water.

A single fiber can be used to transport light both to and from the sample. Optical arrangements for implementing this are shown in Figure 1. However, while this arrangement conserves fiber and provides a well-defined reproducible geometry, it is subject to high levels of stray light arising from reflections at interfaces where there is a change in refractive index. Fluorescence can be resolved from stray light using a monochromator or filter because it occurs at longer wavelengths than the stray light. However, the quality of the required optics is higher when fluorescence has to be measured in the presence of high levels of stray light.
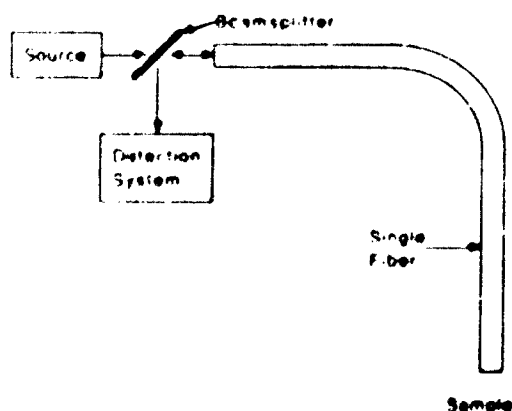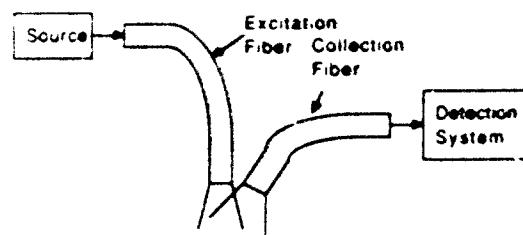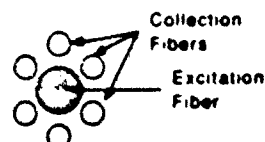

Figure 1. Schematic of arrangement for single fiber measurements

Schematic of system using separate fibers to conduct light to and from the sample. The two fibers are at an angle relative to each other to maximize overlap between the zone illuminated by the excitation fiber and the zone collected by the collection fiber.

Schematic of arrangement in which sample is illuminated by a single large excitation fiber surrounded by several collection fibers.

Figure 2. Separate fibers used to conduct light to and from the sample.

For in-situ ground-water monitoring, it is probably wiser to use separate fibers to conduct light to and from the spectrometer as shown in Figure 2. An experimental comparison of single vs dual fiber arrangements has shown that fluorescence intensities observed for a single fiber measurement are not significantly greater than those observed using a dual fiber arrangement (Louch and Ingle 1988). As shown in Figure 2, collection efficiencies are maximized during emission spectroscopy by holding the two fibers at an angle relative to each other such that there is maximum overlap between the cone of radiation excited by the fiber from the source and the cone of radiation accepted by the fiber leading to the detection system (Plaza et al. 1986). Intensity can be further enhanced by surrounding the excitation fiber with several return fibers, as shown in Figure 2 (Schwab and McCreery 1984, Plaza et al. 1986).

DIRECT SPECTROSCOPY

Because contact with the sample is not required, direct spectroscopic detection of ground-water contaminants is the most attractive approach to in-situ monitoring where applicable. Several types of spectroscopic measurements can be implemented through fibers. Measures that can be taken to enhance sensitivity

generally increase the measurement time and thus cannot be implemented with the cone penetrometer. Various forms of spectroscopy are considered below.

Near infrared spectroscopy

Near-infrared (NIR) spectra are due to weak overtone and combination vibrational bands. Although they appear weak and featureless, they can be recorded at very low noise levels. This makes it possible to use multivariate statistical methods to enhance small spectral differences. This type of measurement is readily implemented through optical fibers (Foulk and Gargus 1987, Weyer et al. 1987, Archibald et al. 1988). However, it is limited to major and minor constituents (components present at levels > 1%) and requires more a priori knowledge of the sample type than would be available if trying to make such measurements directly with the cone penetrometer. This method is not suitable for in-situ plume monitoring.

Raman spectroscopy

Raman spectroscopy is most frequently conducted at wavelengths well out in the visible where optical fibers transmit efficiently. Although Raman spectra have been measured in situ through fibers (Schwab and McCreery 1984, Archibald et al. 1988, Lewis et al. 1988, Leugers and McLachlan 1989), the detection limits are on the order of 1% and are not low enough to detect typical contaminant levels in plumes. Detection limits for phenols in the mg/L range have been obtained using conventional Raman spectroscopy (Marley et al. 1985). A special cell with a 1-m path length coupled to fiber optics has been used to increase the in-situ sensitivity of detection for normal Raman scatters to approximately 1 mg/L (Schwab and McCreery 1987). Resonance Raman spectroscopy is capable of significantly lower detection limits (Schwab and McCreery 1987). However, resonance Raman spectroscopic analysis of ground-water contaminants would be difficult technically and expensive because it requires 1) laser excitation in the ultraviolet, 2) a double or triple monochromator to resolve a weak signal from a much stronger signal at nearby wavelengths, and 3) ultrasensitive light detection equipment.

Interaction with a metal surface greatly enhances the Raman effect and allows compounds to be detected at much lower concentrations than possible with conventional Raman spectroscopy (Carrabba et al. 1987). Because this technique, known as surface enhanced Raman spectroscopy, requires interaction between the analyte and a surface, it is considered below as a spectroscopic technique coupled to a chemical indicator. The "indicator" is the surface that enhances the Raman effect.

The advantages of Raman spectroscopy for in-situ detection are that it can be applied to aqueous solutions and can detect any organic contaminant. Dow Chemical Company has developed in-situ Raman spectroscopy for process control applications (Leugers and McLachlan 1989). However, it is limited to constituents present at > 1%.

Laser-induced fluorescence

Laser-induced fluorescence (LIF) is by far the most promising of the direct forms of spectroscopy that can be implemented through fiber optics. Fluorescence methods are inherently sensitive, capable of measuring concentrations in the part-per-billion range. A laser provides intense highly collimated excitation radiation that illuminates a precise area and can be efficiently coupled into an optical fiber.

Of the four types of contaminant plumes considered in this report, LIF is applicable only to petroleum fuels, responding to aromatic hydrocarbons. Heavy metals, chlorinated and unchlorinated aliphatic hydrocarbons, and nitroaromatic hydrocarbons do not fluoresce. Chlorinated aromatics may fluoresce weakly but the presence of chlorine substituents reduces the efficiency of fluorescence. At this point, the possibility of in-situ fluorimetric detection of chlorinated aromatics remains to be demonstrated.

Benzene, toluene and xylenes are the principal aromatic components of petroleum fuels. Naphthalenes and other higher aromatics may occur in lesser amounts but still at a level readily detected by fluorescence. However, because higher aromatics are not as soluble in water as other components of petroleum fuels, it is to be expected that they will not migrate as rapidly in ground water. Dyes added to oils would also migrate at their own unique rate. Therefore, LIF techniques based on detection of higher aromatics or dyes may not adequately represent plume distribution. The author's opinion is that LIF techniques for mapping petroleum plumes are properly focused on detection of single-ring aromatics even though, instrumentally, this is far more challenging than detecting higher aromatics which fluoresce with greater efficiencies at longer wavelengths.

The feasibility of detecting single-ring aromatics by LIF coupled to fiber optics has been demonstrated (Chudyk et al. 1985). The source was a frequency quadrupled Nd-YAg laser emitting at 266 nm. Radiation was coupled into a 0.60-mm core diameter plastic-clad silica fiber. Separate fibers at an angle of 22° were used to conduct light to and from the sample. Fiber lengths up to 25 m were used. At the excitation wavelength, 266 nm, the attenuation of plastic-clad silica is approximately 500 dB/km. Experimentally the trans-

mittance of 25 m of 0.60-mm core diameter fiber was found to be about 0.04.

Detection limits depend on the particular compound and the measurement conditions. However, they are well down in the part-per-billion range using a filter with maximum transmittance at 320 nm to resolve fluorescence. Typically, measurements required 3 to 5 minutes, corresponding to approximately 5000 laser shots to build up a large integrated intensity value. However, this could easily be shortened, although it would necessarily involve some degradation in the detection limit. Intensities measured by LIF have been compared to the total aromatic content of gasoline measured by gas chromatography at a series of sites, including 12 gasoline stations, two manufacturing companies and one chemical company (Chudyk et al. 1989). The correlation between the two methods is poor, with differences exceeding an order of magnitude on many samples. In particular, LIF gave higher results on samples on which gas chromatography measured low aromatic concentrations. While the origin of the discrepancies is uncertain, the pattern of the data suggest that there may be a background signal due either to natural fluorescence in the sample or increases in stray light levels resulting from the highly scattering nature of the sample.

Although LIF shows promise for direct in-situ detection of hydrocarbon plumes, actual performance will have to be established in practice in comparison to other methods.

Field LIF measurements made to date involve a single intensity measurement. One way of enhancing the information content is to measure intensities at multiple wavelengths. Research to develop the instrumentation technology to do this is currently underway at North Dakota State University (Gregory Gillespie, Principal Investigator) and Tufts University (Jonathan Kenny, Principal Investigator).

Refractive index detection

A variety of methods may be used to optically sense refractive index (Bobb et al. 1989). One approach is to measure the intensity of light reflected at the end of a fiber (Meyer and Fesley 1987). This could be readily implemented for real time in-situ refractive index measurements with the cone penetrometer. However, it might be subject to error due to extraneous light reflected back into the fiber by material outside the fiber. An in-situ refractive index would indicate whether or not the cone penetrometer was in contact with water. It would also be useful in detecting pure contaminant or high levels (> 0.1 to 1%) of contaminant. It would not provide any information as to the identity of the contaminant since all organic contaminants of significance have refractive indices greater than that of water.

SPECTROSCOPIC TECHNIQUES COUPLED TO CHEMICAL INDICATORS

Petroleum fuels and other petroleum-derived products with aromatic components are the only type of ground-water contaminants amenable to direct spectroscopic detection. Current research to develop methods for in-situ detection of other types of plumes has concentrated on systems involving an "indicator" phase that somehow interacts with the analyte to enhance its spectroscopic detectability. Inevitably, time is required for this interaction to take place. While the length of time varies from system to system, none of the in-situ techniques based on indicators is fast enough to be incorporated into the cone penetrometer to provide a real-time continuous profile of concentration vs depth. They would have to be used with the other sample modes of the site characterization and analysis penetrometer system.

Nitro compounds

Amine-containing membranes

Zhang et al. have developed a primary amine containing poly(vinyl chloride) (PVC) membrane that reacts with 2,4,6-trinitrotoluene (TNT) and other polynitroaromatics to form a brown product (Zhang et al. 1989a, Zhang et al. 1989b). The absorption maximum for membranes exposed to TNT is at 510 nm. Because the absorption spectra of the product differs for various polynitroaromatics, the membrane could potentially be used to distinguish different explosives in a mixture.

Formation of the brown product is irreversible. The measured parameter is the rate of color formation. For a typical membrane formulation with a thickness of 0.36 mm, the initial rate of color formation is 0.001 absorbance unit per ppm TNT per minute, when membranes are exposed to aqueous TNT standards (Zhang et al. 1988b). This is independent of membrane area. The detectability depends on the length of time between exposing the membrane to TNT and measuring the membrane absorbance. To get the detection limits below 1 ppm, a typical plume level, it is necessary to wait at least 10 minutes (assuming the minimum detectable change in absorbance is 0.010). This is too long to allow the membrane to be used for real-time detection with the cone penetrometer, although it could be used with the attached sampling mode.

Slow diffusion in the PVC membrane is the reason that the TNT-sensitive membrane responds so slowly. In principle, the same reagent system could be formulated in a nonviscous liquid that could be held in place by a thin TNT-permeable membrane. However, successful development of such a system is uncertain.

4

Although the response time might be improved relative to the PVC membrane, it is almost certainly would not be fast enough to allow continuous profiling with the cone penetrometer.

The color change occurring in PVC membranes has been measured through a single optical fiber (Zhang and Seitz 1989, Zhang et al. 1989a). However, this measurement is subject to relatively high levels of stray light due to reflection at interfaces where there is a change in refractive index. For reasons discussed above, the two-fiber arrangement shown in Figure 2 would be preferred. The measured parameter is the rate at which the ratio of intensity at 824 nm to the intensity at 500 nm increases. Because the brown product does not absorb 824-nm light, this wavelength serves as a reference to compensate for variations in optical properties when different PVC membranes are coupled to the fiber.

Because the measurement is based on absorption, absolute intensity levels are considerably higher than they are for fluorescence. A field instrument capable of making this measurement could be constructed at modest cost (ca. $2000–$5000) using LEDs as light sources. However, such an instrument has yet to be constructed. The entire system would have to be subject to a rigorous evaluation in the field before it could be considered sufficiently reliable for routine use.

The membrane has been shown to respond reliably to TNT in munitions wastewater samples. There is no detectable blank response when membranes are exposed to uncontaminated ground water. The chemical reaction that is believed to be responsible for formation of the brown product is specific for polynitroaromatics. In short, all available evidence suggests that the membrane is suitable for field use but it would be strongly advisable to test its response on a larger number of samples.

Fluorescence quenching

The author of this report is currently investigating an alternative approach to the detection of nitrated organics based on fluorescence quenching. Pyrenebutyric acid is incorporated into plasticized cellulose acetate membranes. These membranes preconcentrate nitrated organics. The presence of nitro compounds in the membrane quenches pyrenebutyric acid fluorescence. The membrane responds to all nitro compounds with its sensitivity depending on the tendency of the nitro compound to partition into the membrane. The fluorescence quenching approach offers the advantage that it responds to hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), an important nonaromatic explosive that is not detected by the PVC membrane.

At this point much more work is required to develop the fluorescence quenching approach. Detection limits

are in the 1- to 10-ppm range and response times are on the order of an hour or more. Even if this approach is successful, it will not be compatible with continuous profiling with the cone penetrometer. It might, however, provide a continuous reversible in-situ response to nitro compounds if the sensor was left in place in ground water.

Volatile halogenated organics

Fujiwara reaction

Efforts to detect halogenated organics have centered on the Fujiwara reaction shown in Figure 3. Halogenated organics react with basic pyridine to form a fluorescent red product. For sensing applications, the reagents are held at the end of an optical fiber and prevented from direct contact with the sample by a hydrophobic membrane that is permeable to volatile halogenated organics. The reaction is irreversible. When response reaches a saturation level, the indicator reagents need to be replaced. Fujiwara-reaction-based sensors cannot be used for continuous in-situ monitoring.

The measured parameter is the rate of produce formation determined either via the rate of increase in fluorescence or absorbance. Initial studies were based on the rate of increase of fluorescence (Milanovich et al. 1986a, Milanovich et al. 1986b). More recently this type of sensor has been used to determine chloroform concentrations in the headspace of contaminated wells (Herron et al. 1990). However, it is difficult to engineer this system to get reproducible responses from sensor to sensor. Fluorescent product initially forms at the interface where the halogenated organic first comes in contact with the reagent. This is followed by movement of the product with the reagent due primarily to convection, which does not occur in a reproducible way. The primary cause of poor reproducibility is variation in the position of the fluorescent product relative to the end of the fiber. This affects both the excitation intensity and
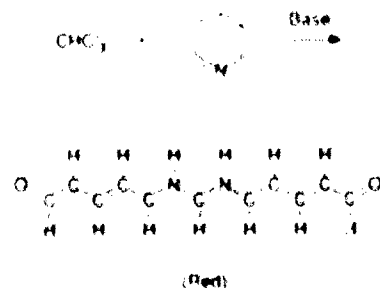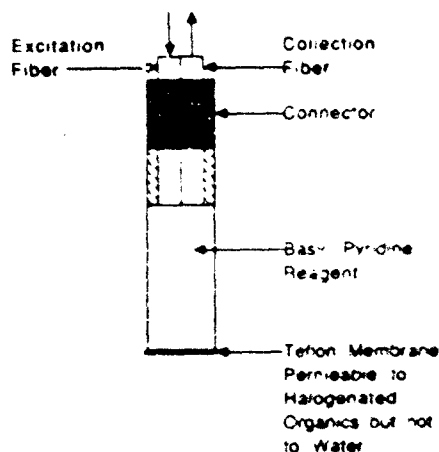

Figure 3. Fujiwara reaction

Figure 4. Schematic of indicator system for detecting halogenated organics. The Teflon membrane serves as a reflector to redirect excitation light back toward the collection fiber.

to develop a LED-based instrument for in-situ absorbance measurements of volatile halogenated organics. *Because the wavelengths required for absorbance measurements of volatile chlorinated hydrocarbons are very similar to the wavelengths for determining polynitro aromatics using an amine-impregnated PVC membrane, a single instrument can be designed to do both measurements.*

The rate of response to chloroform is 0.15 absorbance unit per ppm per minute with a lag time of less than one minute (Angel et al. 1990). This approaches the response times required for continuous profiling with the cone penetrometer. Since the reaction is irreversible, the measured parameter in a continuous profiling experiment would have to be the slope of the response curve, i.e., the change in absorbance per unit change in time. However, there is a dynamic range problem. When the absorbance exceeds 1.00, the measurement is approaching saturation and the slope changes. Once this point is reached, the sensor is no longer viable.

A possible alternative approach to profiling would be to use multiple indicator phases at various distances from the end of the cone penetrometer as shown schematically in Figure 5. When the penetrometer had reached maximum depth, all indicator phases would be exposed to vapor. The response for each indicator could be measured on a rapid sequential basis using a single spectrometer.

Polymers have been added to increase the viscosity of the Fujiwara reagent and reduce the extent of convective mixing, which affects the reproducibility of fluorescence measurements (Herron et al. 1990)

the efficiency with which the fluorescence is collected.

Fluorescence measurements are also subject to saturation due to the "inner filter effect." As red product accumulates, it absorbs a significant fraction of the excitation radiation, which causes the observed fluorescence to be attenuated.

Recently, the possibility of sensing volatile halogenated organics by measuring the increase in the absorbance of the red product has been demonstrated using separate fibers to conduct light to and from the Fujiwara reagent (Angel et al. 1990). The optical arrangement of the reagent phase is shown in Figure 4. In this arrangement the Teflon membrane serves as a reflector to redirect the incident radiation back toward the fiber leading to the detection system. The absorbance approach offers several important advantages. Sensor-to-sensor reproducibility is greatly improved. One reason is that, in the absorbance mode, all absorbing molecules in the optical path affect the observed signal equally, independent of how far they are from the end of the fiber. Another reason is that the measured parameter is the ratio of intensity at 530 nm, which the red product absorbs strongly, to the intensity at 610 nm, which is not absorbed. The use of a ratio measurement compensates for variability in source intensity and the optical characteristics of the indicator phase, most notably variations in the position of the reflecting surface relative to the ends of the two fibers.

The absorbance measurement also requires much less intensity. This not only minimizes photodegradation as a source of error but also substantially simplifies instrumentation requirements. The investigators plan
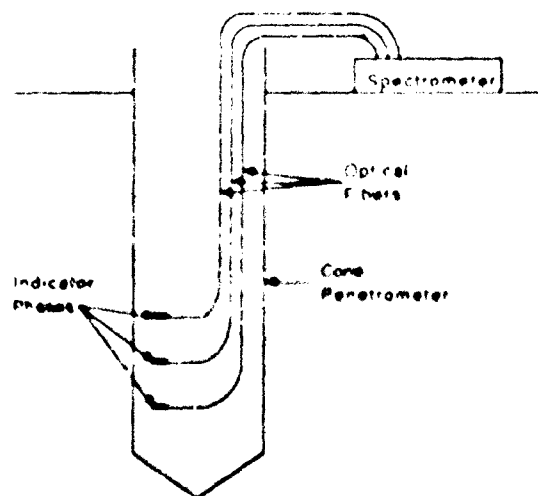

Figure 5. Schematic of arrangement for making several measurements at different depths at the same time

Refractive index

Trichlorethylene (TCE) in water and air has been detected through fiber optics based on a change in refractive index (Oxenford et al. 1989). The cladding is stripped from the core of a fiber and replaced by a coating that has an affinity for TCE. TCE causes a change in the refractive index of the coating, which affects the intensity of light transmitted through the fiber. This approach has been more fully characterized as a method for detecting hydrocarbon contaminants (Klainer et al. 1988). Because it is reversible, the sensor could be left in place in ground water and used for continuous in-situ monitoring. However, further work is required to characterize this approach.

Another possible approach to in-situ detection of halogenated hydrocarbons (and other species) is to apply an RF discharge or an electrical spark to a sample at the tip of an optical fiber. Preliminary experiments have demonstrated response to chlorine-containing compounds (Griffin et al. 1989). However, further work is required before the feasibility of this approach can be evaluated.

## Hydrocarbons

Refractive index

Hydrocarbons in water and air have been detected based on changes in refractive index (Kawahara et al. 1983). The core of an optical fiber is coated with a layer that interacts with hydrocarbons, undergoing a change in refractive index. This in turn affects the intensity of light propagated through an optical fiber. Maximum sensitivity to small changes in refractive index is achieved by designing the system so that the refractive index of the coating is only slightly lower than the refractive index of the core. Intensities propagated through the fiber can be measured directly by placing a source and a detector at opposite ends of the fiber. As shown in Figure 6a, the coated section of fiber can be coiled to make a relatively small sensing element. Because light penetrates into the coating for only a distance on the order of a couple wavelengths, it is easy to make the coating thick enough so that the light does not directly interact with the sample and is not affected by turbidity.

An alternative arrangement for making the measurement is shown in Figure 6b. The coating is placed on a short length of fiber right near the end, and a fluorophor is attached directly at the end (Klainer et al. 1988). The measured parameter is the intensity of fluorescence. The advantage of this arrangement is that the sensing element is at the end of a fiber and can be inserted directly into the sample.

The sensitivity of this approach to a particular compound depends on the affinity of the coating for a
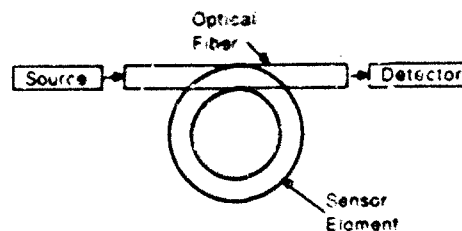
a. Source and detector at opposite ends of the fiber
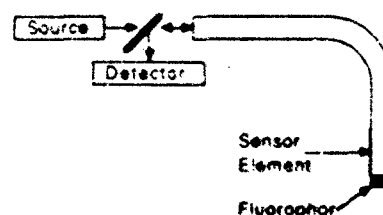
b. Source and detector at the same end of the fiber.

Figure 6. Schematic of arrangement for refractive-index-based sensors.

particular compound and the magnitude of the change in refractive index when the compound partitions into or onto the phase. In general, the less soluble a compound, the more strongly it will partition into an organic coating and the more sensitively it can be detected. A particular coating will be selective for a class of compounds, e.g., aliphatic hydrocarbons, rather than responding to a particular compound. Up to a point, sensitivity can be enhanced simply by coating a greater length of fiber. However, a point will be ultimately reached where sensitivity will be limited by thermal fluctuations in refractive index.

A sensor for oil in water has been developed based on the above principle (Kawahara et al. 1983). The core of a fused silica fiber is reacted with octadecylsilane to produce a lipophilic surface which adsorbs hydrocarbons. The sensor is more sensitive to aromatic hydrocarbons because they have higher refractive indices than aliphatic hydrocarbons. The detection limit depends on both the refractive index of a compound and its affinity for the modified surface. The detection limit for crude oil was 1 mg/L. However, for many other compounds like xylenes it was significantly higher. The measurement was made with the transmission arrangement shown in Figure 6a using a helium-neon laser as the source.

Gasoline vapors have been detected using the optical arrangement shown in Figure 6b (Klainer et al. 1988)

Response is reversible but quite slow. The response for 24-hour equilibration is considerably greater than for 3-hour equilibration, indicating that the sensor is far from equilibrium after 3 hours. The sensor responds to levels as low as 1 μL gasoline/L air. It is not clear how this translates to response to hydrocarbons in water.

In general, sensors in which the target contaminants interact with a coating to produce a refractive index change are too slow to be used for continuous profiling with the cone penetrometer. However, because response involves partitioning rather than a chemical reaction, it is inherently reversible. Such a sensor could potentially be placed in the proper location with the cone penetrometer and used for continuous monitoring. However, the sensitivity levels may be marginal for such an application. Further research and development would have to be done on the preparation and evaluation of such sensors to establish that they could be used for continuous in-situ ground-water monitoring. Although the fiber optic gasoline sensor is or will be available commercially, its primary application would be to look for relatively high concentrations of gasoline near a contamination source rather than the lower levels that would be found in a ground-water plume.

Environment sensitive fluorescence

A fiber-optic sensor for gasoline vapors has been prepared by incorporating an environment-sensitive fluorophor in a siloxane polymer at the tip of a single optical fiber (Wall et al. 1989). Gasoline vapors partition into the polymer, modifying the macroenvironment of the fluorophor and causing an increase in fluorescence intensity and a shift in the emission maximum to shorter wavelength. The response of this sensor has yet to be characterized in depth. It is doubtful that it will respond rapidly enough to be useful for continuous profiling with the cone penetrometer. While response is inherently reversible, it would have to be established that the fluorophor is sufficiently stable for long term use. While the concept is interesting, further work is required to determine whether it could be applied in a practical context.

Surface Enhanced Raman Spectroscopy (SERS)

Adsorption on metal surfaces greatly enhances the Raman effect. The possibility of using this effect for in-situ analysis of ground water contaminants is under investigation (Carrabba et al. 1987, Carrabba 1988, Carrabba et al. 1988, Vo Dinh et al. 1988). The system consists of an electrochemical cell designed so that analyte adsorbs on a silver electrode positioned so that compounds on the surface are efficiently excited. This approach offers several attractive features. It can be applied to any organic contaminant. In addition to spec-

troscopic selectivity, electrochemical selectivity can be achieved by taking advantage of variations in the potential dependence of adsorption for different compounds. Sensitivity can be enhanced by allowing time for analyte to accumulate at the electrode. Because electrochemical cycling can be used to renew the surface, it can be used for several sequential measurements in situ.

Design aspects of a SERS/electrochemistry system for in-situ measurements have been addressed, and several proof-of-principle experiments have demonstrated its attractive features (Carrabba et al. 1987). Nevertheless, the challenges of rendering this approach practical in a field context are formidable. While exciting progress has been made in improving detection limits, it still remains to be shown that SERS/electrochemistry can detect contaminants in ground water at the 10- to 100-ppb level common for many samples. The transition from laboratory measurements of prepared samples to field measurements of contaminants in ground water will almost certainly compound the sensitivity problem. Samples that fluoresce will be subject to high background signals. Other samples may contain components that adsorb on the electrode and interfere with the electrochemistry.

It will also be difficult to develop field instrumentation that performs as well as laboratory instrumentation. Raman spectroscopy requires that a weak signal be measured in the presence of a much larger signal at a nearby wavelength. In the laboratory experiments to demonstrate SERS/electrochemistry, a triple monochromator was used to resolve the signal from the nearby Rayleigh scatter. This is not only expensive but delicate and not readily deployed in the field.

The time scale of SERS/electrochemistry depends on the desired sensitivity but is on the order of minutes or more. It includes time to allow analyte to accumulate on the electrode surface as well as time to acquire the spectral data with adequate signal to noise.

Currently, further research must be completed before SERS/electrochemistry can be considered a serious candidate for practical in-situ contaminant measurements in ground water. Even if this technique is successfully developed, it will not be compatible with the cone penetrometer because it cannot make measurements on the required time scale.

Immunosensing

Immunochemical methods are based on the highly selective interaction between an antibody and an antigen. An in-situ immunochemical method for benzo[a]pyrene has been developed by immobilizing antibody to benzo[a]pyrene on the end of an optical fiber (Vo Dinh et al. 1987, Tromberg et al. 1988). The measured parameter is the rate of increase in

benzo(a)pyrene fluorescence as it binds to an antibody. The detection limit was subanomolar for a 15-minute incubation time.

Nonfluorescent analytes can be detected via the rate at which they displace fluorophor-labeled antigens from antibodies immobilized at the tip of an optical fiber (Anderson and Miller 1938). The measured parameter in this case is the rate at which fluorescence intensity decreases due to displacement. The time scale of these measurements is on the order of minutes, too long to be implemented on the downstroke of the cone penetrometer but the measurements may be taken on the upstroke or read on a separate attached monitor. They are specific to particular compounds rather than responding to a class of compounds. The approach is generic for all compounds against which antibodies can be prepared. This includes substituted aromatics like TNT and multiring compounds like benzo(a)pyrene. Current research is directed at developing immunochemical methods for tetryl, benzene, dieldrin and para-chlorophenylmethylsulfone in environmental samples. The instrumentation used for in-situ measurements has used an argon ion laser as the source with a monochromator to resolve fluorescence from scattered excitation radiation.

Detection of metal ions and cyanide

There have been several reports of optical in-situ measurement of metal ions (Saari and Seitz 1983, Zhujun and Seitz 1985, Lieberman et al. 1987, Inman et al. 1989, Suzuki et al. 1989). The indicator is a ligand with fluorescence characteristics that change upon metal ion binding. Most systems have involved nonfluorescent ligands that form fluorescent complexes. These systems are limited to metal cations that form fluorescent complexes. Of the important metal ion contaminants, Cd(II) can be detected by this approach. Since detection limits are on the order of 10 ppb, the method has sensitivities approaching that required for groundwater analysis. However, Pb(II), Hg(II) and Cr(III) do not form fluorescent complexes.

Selectivity depends on the relative affinity of the ligand for various metal ions. Response is inherently pH dependent for most systems reported to date, because the metal ion has to displace one or more protons to form a complex with the indicator ligand.

None of the metal ion sensing systems reported to date meets the requirement for detecting ground-water contaminants. However, in principle, it should be possible to find a system for detecting heavy metal cations. It would have to be based on absorbance rather than fluorescence in order to get response to the metal ions that do not form fluorescent complexes. Sensitivity can be enhanced by using a ligand with a high affinity for metal ions and allowing time for metal ions to accumu-

late in the indicator phase. However, as with other indicator systems, there will be a tradeoff between sensitivity and time. While the exact time required would depend on the specifics of a system, the author estimates that it would be on the order of 10 to 30 minutes. Almost certainly it would be too long to be implemented for real-time sensing with the cone penetrometer.

The simplest approach for developing a metal ion sensor is to immobilize the indicator on a solid phase at one end of an optical fiber. A more powerful approach is to design the system to provide a constant supply of indicator to the tip of the fiber. Since the indicator is constantly renewed, photodegradation is much less of a problem. Also sensors can be designed to respond continuously on a steady state basis. A pressurized membrane indicator system has been used to supply indicator to a fluorigenic fiber-optic metal ion sensor system (Inman et al. 1989). Another attractive approach is to use a controlled release polymer to provide a constant supply of indicator to a sensor. Although this has not been used with metal ion sensors, it has been successfully implemented with pH indicators (Luo and Walt 1989).

Because metal oxyanions do not form complexes, an indicator system for dichromate would have to be based on a different principle. To date there have not been any efforts to develop a system for in-situ optical detection of dichromate.

One of the earliest reports of fiber optic chemical sensors described an indicator for cyanide (Hardy et al. 1985). However, emphasis was on demonstrating a principle and very little detail was provided. There has not been any further work on cyanide.

The Office of Naval Research has recently made the development of trace metal biosensors a high priority research area. Research funded by this initiative may lead to improved methods for in-situ metal analysis that can be applied to contaminant plumes.

NONSPECTROSCOPIC TECHNIQUES

Hydrocarbons in fuel plumes and halogenated organic solvents cannot be determined electrochemically. Aromatic nitro compounds have been detected voltammetrically at concentrations approaching those occurring in contaminated ground water (Whitnack 1963). Pb(II) and Cd(II) are readily determined by electrochemical methods. The sensitivity of direct electrochemical methods, e.g., pulse voltammetry, approaches the level required for contaminated ground water. Sensitivity can be further enhanced by using the technique of anodic stripping voltammetry. A metal ion is

reduced at an electrode under controlled conditions for a known period of time. The voltage is then scanned anodically and the current required to reoxidize the metal ion is measured.

Voltammetric methods have fallen into disrepute in recent years. They are subject to interferences and surface contamination. Other analytical approaches are considerably more "rugged" and do not require as high a degree of operator expertise as electrochemistry. For this reason, there has not been significant activity in applying voltammetric methods for in-situ detection of metal ions in spite of the fact that these should be applicable in favorable contexts.

SUMMARY

This report describes in-situ analysis of groundwater contaminants by methods that can potentially be implemented with the cone penetrometer, a device for rapid deployment from the surface down to ground water. Sensors can be mounted directly in the penetrometer for real-time analysis during ground penetration. Alternatively, the site characterization and analysis penetrometer system (SCAPS) allows attached/disattached (drop-off) modes of sampling/monitoring. The report emphasizes detection limits since they define the detectable outer limits of a contaminant plume. Several types of spectroscopic measurements including fluorescence, Raman and near-infrared absorption are readily implemented in situ through fiber optics. However, of these, only laser-induced fluorescence (LIF) has the sensitivity required to detect typical contaminant levels in ground-water plumes with response times short enough for real-time detection with the cone penetrometer. Although LIF has been applied for in-situ detection of hydrocarbons, further development work is required to establish the type of response that is observed and to correlate it with hydrocarbon levels. LIF is not applicable to other types of contaminants because they do not fluoresce.

Indicator systems based on irreversible reactions to form absorbing products have been developed for sensitive (i.e., detection limits as low as 10 μg/L) in-situ detection of chlorinated hydrocarbons and polynitroaromatic hydrocarbons. The instrumentation requirements are quite modest. However, because the time scale of the measurement is on the order of minutes for the chlorinated hydrocarbons and hours for polynitroaromatics, these systems are not compatible with real-time operation of the cone penetrometer although they could be used with the SCAPS.

Reversible refractive-index-based detection has been demonstrated for hydrocarbons in gasoline and for

chlorinated hydrocarbons. Response times are too slow for the cone penetrometer because it is necessary to preconcentrate analyte to get detection limits down to the mg/L level. With further development, refractive-index-based detection may provide a method for continuously detecting elevated levels of organic contaminants in ground water.

Metal cations may be detected spectroscopically by reacting them with indicators to form colored complexes. However, this type of detection requires considerable further work before it can be adapted to in-situ detection of metal cations in ground water. In-situ detection of anions such as cyanide and dichromate is a difficult problem that is not currently being addressed.

Ion selective electrodes can detect Pb(II), Cd(II), Cu(II) and cyanide at levels approaching 0.10 mg/L but are subject to drift and do not respond to metal ion or ligands in complex ions. Amperometric methods can be used to detect heavy metal cations such as Pb(II) and Cd(II). However, preconcentration techniques are required to detect levels below about 0.5 mg/L. Electrochemical methods are subject to error due to contamination of the electrode surface and require a high degree of operator skill. Surface acoustic wave detectors could potentially be used to detect volatile contaminants in situ although to date no work has been done in this area.

LITERATURE CITED

A. gel, S.M. (1987) Optrodes: Chemically selective fiber-optic sensors. *Spectroscopy*, 2: 38–48.

Angel, S.M., L.F. Katz, D.D. Archibald, L.T. Lin and D.E. Honigs (1988) Near-infrared surface-enhanced Raman spectroscopy. Part I: Copper and gold electrodes. *Applied Spectroscopy*, 42: 1327–1329.

Angel, S.M., M. Nugent, K. Langry and T.J. Kulp (1990) Development and applications of fiber-optic sensors. In *Proceedings of American Chemical Society Symposium on Chemical Sensors and Microinstrumentation, Los Angeles*, in press.

Anderson, F.P. and W.G. Miller (1988) Fiber optic immunochemical sensor for continuous, reversible measurement of phenytoin. *Clinical Chemistry*, 34: 1417–1421.

Archibald, D.D., L.T. Lin and D.E. Honigs (1988) Raman spectroscopy over optical fibers with the use of a near-IR FT spectrometer. *Applied Spectroscopy*, 42: 1558–1563.

Archibald, D.D., C.E. Miller, L.T. Lin and D.E. Honigs (1988) Remote near-IR reflective measure-

ments with the use of a pair of optical fibers and a Fourier transform spectrometer. *Applied Spectroscopy*, 42: 1549–1558.

Bobb, L.C., H.D. Krumboltz ar d J.P. Davis (1989) Optical fiber refractometer. In *Proceedings of The Society of Photo-Optical Instrumentation Engineers*, 990: 164–169.

Carrabba, M.M. (1988) Surface-enhanced Raman spectroscopy (SERS): An existing or emerging chemical sensing technology? In *Proceedings of the Department of Energy In-Situ Characterization and Monitoring Technologies Workshop* DOE/HWP-62.

Carrabba, M.M., R.B. Edmonds and R.D. hauh (1987) Feasibility studies for the detection of organic surface and subsurface water contaminants by surface-enhanced Raman spectroscopy of silver electrodes. *Analytical Chemistry*, 59: 2559–2563.

Carrabba, M.M., R.B. Edmonds, P.J. Marren and R.D. Raub (1988) The suitability of surface enhanced Raman spectroscopy (SERS) to fiber optic chemical sensing of aromatic hydrocarbon contamination in ground water. Presented at Symposium on Field Screening Methods for Hazardous Waste Site Investigations, Las Vegas, Nevada.

Chudyk, W.A., M.M. Carrabba and J.E. Kenny (1985) Remote detection of ground-water contaminants using far-ultraviolet laser-induced fluorescence. *Analytical Chemistry*, 57: 1237–1242.

Chudyk, W., K. Pohlig, N. Rico and G. Johnson (1989) Ground-water monitoring using laser fluorescence and fiber optics. In *Proceedings of the Society of Photo-Optical Instrumentation Engineers*, 990: 4545–4548.

Drexhage, M.G. and C.T. Moynihan (1988) Infrared optical fibers. *Scientific American*, Nov: 110–116.

Eccles, L.A. and D. Eastwood (1989) Rationale for in situ environmental monitoring with fiber optics. In *Proceedings of the Society of Photo-Optical Instrumentation Engineers*, 990: 30–36.

Foulk S. and A.G. Gargus (1987) Fiber optic spectroscopy and multivariate analysis for in situ chemical monitoring. *American Laboratory*, December: 52–53.

Griffin, J.W., K.B. Olsen, B.S. Matson, D.A. Nelson and P.A. Eschbach (1989) Fiber optic spectrochemical emission sensors. In *Proceedings of the Society of Photo-Optical Instrumentation Engineers*, 990: 55–68.

Hardy, E.E., D.J. David, N.S. Kapany and F.C. Unterleitner (1985) Coated optical waveguides for spectrophotometry of chemical reactions. *Nature*, 257: 666.

Herron, N.R., S. Simon and L.A. Eccles (1990) Remote detection of organochlorides with a fiber-optic based sensor III: Calibration and field evaluation of an improved chloroform fiber optic chemical sensor with a

dedicated portable fluorimeter. *Analytical Instrumentation*, in press.

Hirschfeld, T., T. Deaton, F. Milanovich and S. Klainer (1983) Feasibility of using fiber optics for monitoring ground-water contaminants. *Optical Engineering*, 22: 527–31.

Hirschfeld, T., T. Deaton, F. Milanovich and S. Klainer (1984) Feasibility of using fiber optics for monitoring ground-water contaminants. EPA Report 600/7-84-067.

Inman, S.M., E.J. Stromvall and S.H. Lieberman (1989) Pressurized memb.ane indicator system for fluorogenic-based fiber optic chemical sensors. *Analytica Chimica Acta*, 217: 249–262.

Kawahara, F.K., R.A. Fiutem, H.S. Silvus, F.M. Newman and J.H. Frazar (1983) Development of a novel method for monitoring oils in water. *Analytica Chimica Acta*, 151: 315–327.

Klainer, S.M., D.K. Dandge, K. Goswami, L.A. Eccles and S.J. Simon (1988) A fiber-optic chemical sensor (POCS) for monitoring gasoline. EPA Report 600/X-88/259.

Leugers, M.A. and R.D. McLachlan (1989) Remote analysis by fiber optic Raman spectroscopy. In *Proceedings of the Society of Photo-Optical Instrumentation Engineers*, 990: 88–95.

Lewis, E.N., V.J. Kalasinsky and I.W. Levin (1988) Near-infrared Fourier transform Raman spectroscopy using fiber-optic assemblies. *Analytical Chemistry*, 60: 2658–2661.

Lieberman, S.H., S.M. Inman and E.J. Stromvall (1987) Fiber-optic fluorescence sensors for remote detection of chemical species in seawater. In *Chemical Sensors* (D.R. Turner, Ed.). *The Electrochemical Society*, 464–475.

Louch, J. and J.D. Ingle (1988) Experimental comparison of single-and double-fiber configurations for remote fiber-optic fluorescence sensing. *Analytical Chemistry*, 60: 2537–2540.

Luo, S. and D.R. Walt (1989) Fiber-optic sensors based on reagent delivery with controlled-release polymers. *Analytical Chemistry*, 61: 174–177.

Marley, N.A., C.K. Mann and T.J. Vickers (1985) Raman spectroscopy in trace analysis for phenols in water. *Applied Spectroscopy*, 39: 628–633.

Meyer, M.S. and G.L. Eesley (1987) Optical fiber refractometer. *Review of Scientific Instruments*, 58: 2047–2048.

Milanovich, F.P., P.F. Daley, S.M. Klainer and L.A. Eccles (1986a) Remote detection of organochlorides with a fiber optic-based sensor II. A dedicated portable fluorimeter. *Analytical Instrumentation*, 15: 347–358.

Milanovich, F.P., D.G. Garvis, S.M. Angel, S.M. Klainer and L.A. Eccles (1986b) Remote detection of

organochlorides with a fiber optic based sensor. *Analytical Instrumentation*, 15: 137–147.

Oxenford, J.L., S.M. Klainer, D. LeGoullon, T.M. Salina, D.K. Dandge and K. Goswami (1989) Development of a fiber optic chemical sensor for the monitoring of trichloroethylene in drinking water. Abstract received from ST&E, Inc., Pleasanton, California.

Plaza, P., N.Q. Dao, M. Jouan, H. Feurier and H. Saisse (1986) Simulation et optimisation des capteurs á fibres optiques adjacentes. *Applied Optics*, 25: 3448–3454.

Saari, L.A. and W.R. Seitz (1983) Immobilized morin as fluorescence sensor for determination of aluminum (III). *Analytical Chemistry*, 55: 667–670.

Schwab, S.D. and R.L. McCreery (1984) Versatile, efficient Raman sampling with fiber optics. *Analytical Chemistry*, 56: 2199–2204.

Schwab, S.D. and R.L. McCreery (1987) Remote, long path length cell for high sensitivity Raman spectroscopy. *Applied Spectroscopy*, 41: 126–130.

Seitz, W.R. (1988) Chemical sensors based on immobilized reagents and fiber optics. *Analytical Chemistry*, 19: 135–173.

Skutnik, B.J., C.T. Brucker and J.P. Clarkin (1988) High numerical aperture silica core fibers for biosensor applications. In *Proceedings of the Society of Photo-Optical Instrumentation Engineers*, 906: 21–25.

Suzuki, K., K. Tohda, Y. Tanda, H. Ohzora, W. Hishihama, H. Inoue and T. Shirai (1989) Fiber-optic magnesium and calcium ion sensor based on a natural carboxylic polyether antibiotic. *Analytical Chemistry*, 61: 382–384.

Tromberg, B.J., M.J. Sepaniak, J.P. Alarie, T. Vo-Dinh and R. Santella (1988) Development of antibody-based fiber-optic sensors for detection of a benzo[a]pyrene metabolite. *Analytical Chemistry*, 60: 1901–1908.

Vo-Dinh T., A. Alak and R.L. Moody (1988) Recent advances in surface-enhanced Raman spectrometry for chemical analysis. *Spectrochimica Acta*, 43B 605–616.

Vo-Dinh, T., B.J. Tromberg, G.D. Griffin, K.R. Ambrose, M.J. Sepaniak and E.M. Gardenhire (1987)

Antibody-based fiberoptic biosensor for the carcinogen benzo(a)pyrene. *Applied Spectroscopy*, 41: 735–738.

Walt, D.R., C. Hunkholm, P. Yuan, S. Luo and S. Barnard (1989) Design, preparation and applications of fiber optic chemical sensors for continuous monitoring. In *Proceedings of American Chemical Society Symposium on Chemical Sensors and Microinstrumentation*, Los Angeles, in press.

Weyer, L.G., K.J. Becker and H.B. Leach (1987) Remote sensing fiber optic probe NIR spectroscopy coupled with chemometric data treatment. *Applied Spectroscopy*, 41: 786–790.

Whitnack G.C. (1963) Determination of trinitrotoluene in warhead exudates by linear sweep polarography. *Analytical Chemistry*, 35: 970–973.

Wolfbeis, O. (1988) Fiber optical fluorosensors in analytical and clinical chemistry. In *Molecular Luminescence Spectroscopy: Methods and Applications-Part II* (S.G. Schulman, Ed.), New York: Wiley Interscience, p. 129–281.

Zhang, Y. and W.R. Seitz (1989) Single fiber absorption measurements for remote detection of 2,4,6-trinitrotoluene. *Analytica Chimica Acta*, 221: 1–9.

Zhang, Y., W.R. Seitz and D.C. Sundberg (1988a) Development of a membrane for in-situ optical detection of TNT. USATHAMA Report AMXTH-TE-CR-88021.

Zhang, Y., W.R. Seitz and D.C. Sundberg (1989a) Single fiber measurements for remote optical detection of TNT. USATHAMA Report CETHA-TE-CR-89102.

Zhang, Y., W.R. Seitz, C.L. Grant and D.C. Sundberg (1989b) A clear, amine-containing poly(vinyl chloride) membrane for in situ optical detection of 2,4,6-trinitrotoluene. *Analytica Chimica Acta*, 217: 217–227.

Zhang, Y., W.R. Seitz, D.C. Sundberg and C.L. Grant (1989b) Preliminary development of a fiber optic sensor for TNT. USATHAMA Report AMXTH-TE-CR-87135.

Zhujun, Z. and W.R. Seitz (1985) An optical sensor for Al(III), Mg(II), Zn(II) and Cd(II) based on electrostatically immobilized 8-hydroxyquinoline sulfonate. *Analytica Chimica Acta*, 171: 251–258.

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestion for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE August 1990	3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE

In-Situ Detection of Contaminant Plumes in Ground Water

5. FUNDING NUMBERS

C: WESAM 89-110

6. AUTHORS

W. Rudolf Seitz

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry
University of New Hampshire
Durham, New Hampshire 03824

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Sponsor:
U.S. Army Toxic and Hazardous Materials Agency
CETHA-TS-D
Aberdeen Proving Ground, MD 21010-5401

Monitor:
U.S. Army Cold Regions Research
and Engineering Laboratory
Hanover, NH 03755-1290

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

Sponsor:
CETHA-TE-CR-90049
Monitor:
Special Report 90-27

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Ground-water contaminants can be detected in situ by making spectroscopic measurements through fiber optics. In addition to direct measurements, it is possible to couple fiber optics with chemical indicators that interact with the contaminants to enhance their detectability. Direct fluorescence measurements have been used to sensitively detect aromatic hydrocarbons in fossil fuels. Direct Raman measurements are also possible but can only detect relatively high concentrations (> 0.1 %). Parts per billion levels of nitroaromatics and halogenated hydrocarbons can be detected using indicators that react to form colored products. The rate at which the absorbance of the colored product increases is proportional to concentration. Refractive index measurements offer a rugged reversible approach to detecting organic contaminants in the low parts per million range. All of these techniques require further development before they can be reliably used on a routine basis. Other spectroscopic techniques are considered in the report but are not considered ready for in-situ ground-water monitoring at this time.

14. SUBJECT TERMS

Contaminant detection
Fiber optics
Ground water
Spectroscopy

15. NUMBER OF PAGES 18

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	